

THE SORPTION OF OXYGEN BY SEVERAL METAL
CHROMITES

DISSERTATION

SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES OF
THE JOHNS HOPKINS UNIVERSITY IN CONFORMITY
WITH REQUIREMENTS FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

BY

LLEWELLYN HEARD

BALTIMORE

1936



Digitized by the Internet Archive
in 2026

https://archive.org/details/IA41547018_0011

THE SORPTION OF OXYGEN BY SEVERAL METAL
CHROMITES

DISSERTATION

SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES OF
THE JOHNS HOPKINS UNIVERSITY IN CONFORMITY
WITH REQUIREMENTS FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

BY

LLEWELLYN HEARD

BALTIMORE

1936

ACKNOWLEDGMENT

The author wishes to thank Professor J. C. W. Frazer for suggesting this problem, and for his constant assistance and encouragement in carrying it to completion.

The author also wishes to thank the members of the Staff of the Department of Chemistry for their valuable advice and instruction in the classroom and laboratory.



THE SORPTION OF OXYGEN BY SEVERAL METAL CHROMITES

LLEWELLYN HEARD

Department of Chemistry, The Johns Hopkins University, Baltimore, Maryland

The study made by C. G. Albert (2) of the sorption of oxygen and of carbon monoxide by a copper chromite catalyst indicated that a similar study of the sorption of oxygen by several metal chromites might be of interest. The opinion that alternate oxidation and reduction of chromite catalysts tended to render them more active had been suggested by limited experience with some chromites, but it was not known whether chromites prepared by other methods would sorb greater or lesser quantities of oxygen. However, a very good basis for surface comparison was at hand, since Lory (3) had arrived at a figure of 4.11×10^{18} surface atoms of chromium per gram of a copper chromite catalyst, this value having been obtained by leaching chromic acid from the oxidized catalyst with boiling water and titrating with sodium thiosulfate.

APPARATUS AND TECHNIQUE

The apparatus and technique employed in making these measurements, as well as the preparation and purification of gases involved, were as described by Albert (2), with the exception that the volume measurements of the catalyst bulb were made, at the several temperatures, with tank nitrogen instead of helium, it having been determined that, as far as this purpose was concerned, no differences could be observed. An oxygen pressure of 350 mm. of mercury was likewise adopted. Sorption data were plotted in terms of cubic centimeters of oxygen sorbed per gram of catalyst versus time in minutes. From the rate isotherms so obtained, energies of activation associated with the sorption process were calculated.

THE CATALYSTS

The general scheme of preparing the catalysts consisted in obtaining a crystalline intermediate of the type $(\text{NH}_4)_2\text{M}(\text{CrO}_4)_2 \cdot 2\text{NH}_3$ (1) (where M is a bivalent metal), drying, decomposing thermally at as low a temperature as possible (200–300°C.), leaching with hot 6 N hydrochloric acid until no further test for metal ion could be obtained, washing, and drying.

While the use of leach-acid may have influenced the catalyst otherwise, the primary purpose was to dissolve any undecomposed material and any

metal oxide present, since the oxide would have been variously subject to reduction by carbon monoxide with consequent inaccurate sorption results.

The chromites studied are regarded as insoluble in concentrated hydrochloric acid, although in their oxidized state, concerning which little beyond conjecture is available, chromic acid may be leached from them by water.

Chromites made in this manner take up water and other liquids. It was the practice, immediately upon sealing them into the system, to raise the temperature to 300°C. and then carefully to evacuate to 1–10 mm. of mercury. Under these conditions from 48 to 72 hours were required to dry them.

The object of using the crystal intermediate method was that uniformity of composition would always be found in pure crystals, giving rise to catalyst reproducibility.

TABLE 1
Conversion temperatures of carbon monoxide by chromites

CHROMITE	LOWEST CONVERSION TEMPERATURE	LOWEST TEMPERATURE OF COMPLETE CONVERSION
	°C.	°C.
CuCr ₂ O ₄	85	185
ZnCr ₂ O ₄	100	210
CoCr ₂ O ₄	68	210
NiCr ₂ O ₄	78	141
BeCr ₂ O ₄	105	186

The catalysts employed were the chromites of copper, zinc, cobalt, nickel, and beryllium. Those of copper, zinc, and cobalt were prepared by the scheme of Briggs (1), but nickel chromite by the same method was so finely divided that it could not be leached with 6 *N* hydrochloric acid without being peptized and carried away in the leach-acid. Its preparation consisted in dissolving nickelous pyridino dichromate (4), NiCr₂O₇·4Py, in concentrated ammonium hydroxide, removing the pyridine layer which separated, and crystallizing. This product required heating to redness before any appreciable decomposition could be observed. The second leaching failed to give a test for nickel. Beryllium chromite was prepared by the thermal decomposition of (NH₄)₂Be(CrO₄)₂. It was a fine gray powder.

For each catalyst the temperature at which conversion of carbon monoxide to carbon dioxide began, and at which it was complete and continuous, was determined in the apparatus described by Lory. These operations established the ranges within which, at 25°C. intervals, sorption measurements should be made. The lower and upper limits are shown in table 1.

Before sealing a catalyst into the system the sample was placed in a Pyrex carbon dioxide trap within an electric resistance furnace and, when the temperature had come to equilibrium at 200°C., a slow stream of tank oxygen was passed over it for 2 hours. The object was to oxidize the catalyst surface completely. After sealing into the system the chromite was reduced in an atmosphere of carbon monoxide prior to making each measurement.

EXPERIMENTAL RESULTS

The data of the sorption of oxygen by the several chromites employed are indicated graphically in figures 1 to 5, inclusive, while the calculated values of E are given in tables 2 to 5.

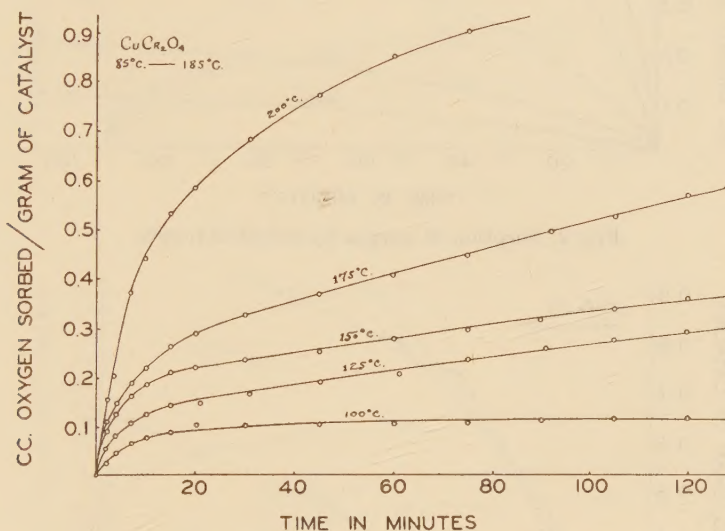


FIG. 1. Sorption of oxygen by copper chromite

It is interesting to note that while this sample of copper chromite sorbed approximately four times the amount of oxygen sorbed by Albert's catalyst, under the same conditions, the values for the energies of activation are in quite good agreement.

A sample of 5.1596 g. of this same batch of copper chromite was brought to 200°C. in a carbon dioxide trap, as indicated above, and a stream of tank oxygen was passed over it for 2 hours. The temperature rose at once to about 600°C., and then gradually fell during the next 10 to 15 minutes. At the end of the treatment the sample was leached with hot water until no further chromium could be found in a drop of the leach-water. It yielded 0.0815 g. of chromium, giving a figure of 1.84×10^{20} surface atoms

of chromium per gram of catalyst, which, divided by Lory's figure, indicates an oxidizable or active surface 44.77 times greater than that shown

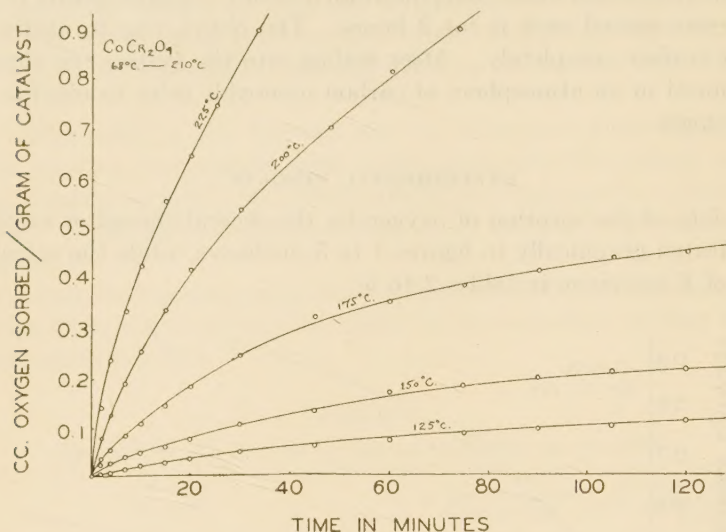


FIG. 2. Sorption of oxygen by cobalt chromite

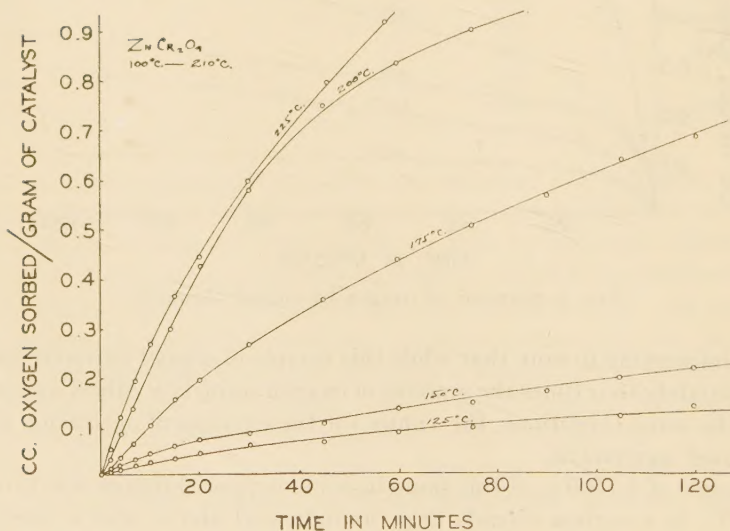


FIG. 3. Sorption of oxygen by zinc chromite

by Albert's catalyst. The apparent discrepancy between the amount of oxygen sorbed by the catalyst within the system at 200°C. and the enormity of the surface indicated by the leaching method is readily explained. The

pressure maintained in the system was 350 mm. of mercury, whereas oxidation prior to leaching was carried out at atmospheric pressure. Thus more

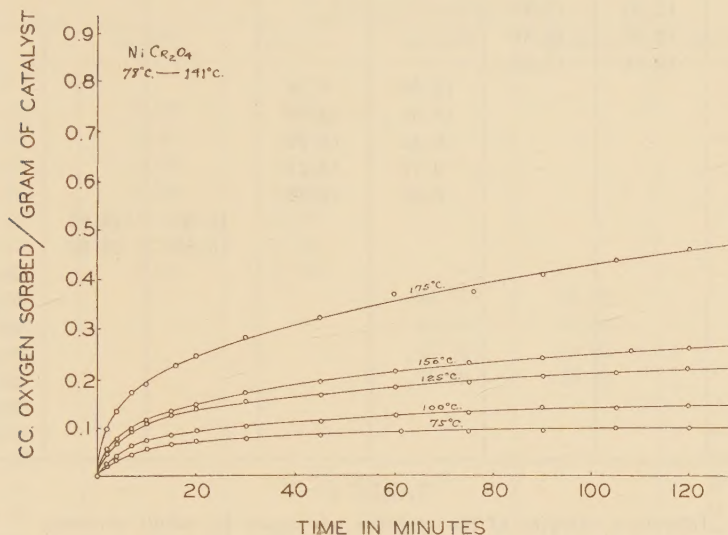


FIG. 4. Sorption of oxygen by nickel chromite

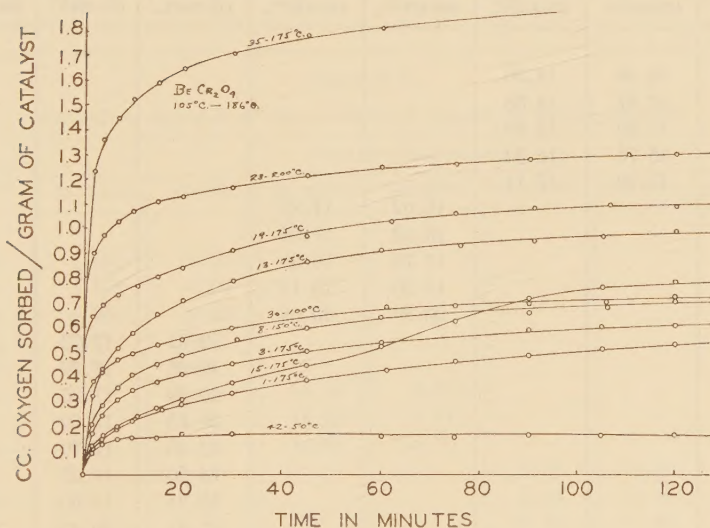


FIG. 5. Sorption of oxygen by beryllium chromite

rapid oxidation accompanied by rapid increase in temperature produced in turn still greater oxidation, both sorption measurement and heat treatment being conducted over identical time intervals. Assuming the forma-

TABLE 2
Activation energies of the sorption of oxygen by copper chromite

AMOUNT SORBED	<i>E</i> (IN KILOGRAM-CALORIES)						
	100-125°C.	100-150°C.	125-150°C.	125-175°C.	150-175°C.	150-200°C.	175-200°C.
cc.							
0.02	15.58	16.94					
0.04	12.63	13.58					
0.06	12.00	11.31					
0.08	12.07	10.87					
0.10	13.44	11.92					
0.14			12.55	8.78			
0.18			18.91	12.66			
0.22			16.41	13.22			
0.26			9.17	13.21			
0.30			6.32	12.08			
0.33					18.36	22.83	
0.36					15.85	22.99	
0.39							33.39
0.42							34.03
0.45							34.19
0.48							35.46
0.51							33.26
0.54							32.42
0.57							31.60

TABLE 3
Activation energies of the sorption of oxygen by cobalt chromite

AMOUNT SORBED	<i>E</i> (IN KILOGRAM-CALORIES)						
	125-150°C.	125-175°C.	150-175°C.	150-200°C.	175-200°C.	175-225°C.	200-225°C.
cc.							
0.02	16.08	14.36					
0.04	13.87	14.58					
0.06	13.80	15.19					
0.08	15.76	16.32					
0.10	17.72	17.11					
0.12			16.92	17.87			
0.14			16.93	17.95			
0.16			17.70	18.39			
0.18			19.20	19.14			
0.20			20.89	20.08			
0.24					19.32	17.22	
0.27					19.86	17.36	
0.30					20.39	17.25	
0.33					20.85	17.59	
0.36					22.06	17.79	
0.39					24.50	18.65	
0.42					25.24	19.60	
0.45					27.51	20.43	
0.50							14.34
0.55							14.53
0.60							14.38
0.65							14.33
0.70							14.34
0.75							14.48
0.80							14.65
0.85							15.05
0.90							15.52

TABLE 4
Activation energies of the sorption of oxygen by zinc chromite

AMOUNT SORBED	<i>E</i> (IN KILOGRAM-CALORIES)				
	125-150°C.	125-175°C.	150-175°C.	150-200°C.	175-200°C.
cc.					
0.02	7.07	8.32			
0.04	8.18	9.72			
0.06	10.59	12.32			
0.08	10.96	14.15			
0.10	11.15	15.09			
0.12	9.80	15.64			
0.14	9.09	14.65			
0.16			24.51	18.89	
0.18			24.94	19.48	
0.20			25.32	19.81	
0.22			25.39	19.93	
0.25					14.65
0.30					15.02
0.35					16.12
0.40					16.69
0.45					17.24
0.50					17.87
0.55					18.59
0.60					18.53
0.70					18.72

TABLE 5
Activation energies of the sorption of oxygen by nickel chromite

AMOUNT SORBED	<i>E</i> (IN KILOGRAM-CALORIES)						
	75-100°C.	75-125°C.	100-125°C.	100-150°C.	125-150°C.	125-175°C.	150-175°C.
cc.							
0.02	1.151	6.33					
0.04	3.378	5.93					
0.06	4.961	6.46					
0.08	11.03	10.17					
0.10	13.91	14.11					
0.12			16.14	9.92			
0.14			18.23	11.77			
0.16			14.51	10.70			
0.18					6.62	13.45	
0.20					7.00	14.12	
0.22					8.42	14.89	
0.24							23.27
0.26							23.54

tion of monomolecular layers in both the Lory and the present form of chromite, there is far from enough information to relate surface to oxygen sorbed over short time intervals.

DISCUSSION

Many of the metal chromites may be prepared through the Briggs' intermediate, and those so prepared have large surfaces as compared with the Lory catalyst.

The energies of activation of those chromites studied compare favorably with the values obtained for copper chromite by Albert.

Because of the peculiar action of beryllium chromite it was not possible to obtain any reliable energy values. The first sorption measurement was conducted at 175°C., and when an effort was made to duplicate the rate isotherm a curve revealing greater sorption resulted. A third run at the same temperature gave a curve lying still higher. Curves representing runs 1 and 3 are shown on the graph as 1-175 and 3-175. A run was then made at 100°C., and no oxygen appeared to be taken up. Half a dozen runs were next made, alternately, at 150°C. and 175°C. Each successive curve fell higher than the preceding one for the same temperature.

After run 13 had been made at 175°C., where sorption occurred to approximately twice the extent in run 1, it was decided that the catalyst might be brought to a condition of maximum sorption by oxidizing it at atmospheric pressure and at 200°C. This treatment caused it to lose temporarily some of its sorptive capacity, and the run which followed, at 175°C., gave a curve lying almost on top of curve 1. Thereafter its sorptive capacity began to increase again, curve 15 indicating this tendency.

Several runs were then made alternately at 175°C. and 200°C.; two of the results are shown in curves 19 and 23. After run 35, at 175°C., when beryllium chromite was sorbing about thirty times the amount of oxygen sorbed by Albert's catalyst and about five times that sorbed by the copper chromite sample used in these measurements, several runs were made at lower temperatures; finally, run 42 was made at 50°C. with the results shown in the graph. It may be remembered that run 4 was made at 100°C. without measurable sorption occurring.

This points to the already-proposed view that alternate oxidation and reduction of a chromite catalyst tends to increase its activity,—certainly in the case of beryllium chromite. It is not known whether more surface was being progressively activated or whether the particles of catalyst were breaking into more finely divided particles. In any event the apparent volume of the catalyst in the tube appeared to be unchanged.

After the beryllium chromite was removed from the system it was retested in the Lory apparatus. The temperature of initial conversion of carbon monoxide to carbon dioxide had fallen to 38°C., while the temperature of complete conversion had risen to 192°C.

REFERENCES

- (1) BRIGGS, S. H. C.: *J. Chem. Soc.* **83**, 394 (1903).
- (2) FRAZER, J. C. W., AND ALBERT, C. G.: *J. Phys. Chem.* **40**, 101-12 (1936).
- (3) LORY, E. C.: *J. Phys. Chem.* **37**, 685-92 (1933).
- (4) PARRAVANO AND PASTA: *Gazz. chim. ital.* **37**, II, 255 (1907).

BIOGRAPHY

The author was born at Macon, Bibb County, Georgia, December 30, 1901.

His high school training was gained at Gordon Military Institute, at Barnesville, Georgia, upon completion of which he enlisted in the U. S. Army for a period of three years.

After his discharge from the Army he entered Emory University, receiving from that institution the degree of Bachelor of Science, in 1928.

During the academic year 1928-29 he taught algebra at the Lanier High School, at Macon, Georgia, and during the period 1929-32 he served as an instructor in the Department of Chemistry at the University of Georgia, at Athens. He was awarded the degree of Master of Science in Chemistry by that institution in 1932.

After serving two years as Professor of Chemistry at the South Georgia State College, at Douglas, Georgia, he resigned in order to enroll in the School of Higher studies at the Johns Hopkins University.

